# Boosting photocatalytic cross-dehydrogenative coupling reaction by incorporating [Ru^II(bpy)_3] into a radical metal-organic framework

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A B S T R A C T

Due to energy-efficient and green processes of photocatalysis, the visible-light-driven photocatalytic organic synthesis has developed greatly in the last decade. The well-known photocatalysts, Ru^II-polypyridyl complexes, have been extensively exploited in the synthesis of various chemicals. However, homogeneity of Ru^II-polypyridyl complexes makes their recycling difficult. Here, we show an effective strategy for boosting photocatalysis by incorporating [Ru^II(bpy)_3] into a radical metal-organic framework (**FJI-Y2**). Recyclable photocatalyst **FJI-Y2** can efficiently catalyze the cross-dehydrogenative coupling reactions of *N*-phenyltetrahydroisoquinoline derivatives with phosphite esters, forming medicinal α-aminoquinoline phosphonates. More importantly, the photocatalytic efficiency of **FJI-Y2** is actually higher than its homogeneous counterpart [Ru^II(bpy)_3]Cl_2, because multiple intermolecular interactions between 1,4,5,8-naphthalenediimide radicals and [Ru^II(bpy)_3] induce optimal photoinduced electron transfer process to expedite chemical conversion and recycling of catalysts. It is envisioned that MOFs containing radicals can be ideal platforms to incorporate more noble-metal photocatalysts for promoting photocatalysis.

## 1. Introduction

Benefitting from sunlight as a sustainable energy source, visible-light-driven photocatalysis is thought to be a clean and energy-efficient process for organic synthesis [1–4]. In the past decades, the Ru^II-polypyridyl complexes as visible light photocatalysts, such as [Ru^II(bpy)_3] (bpy = 2,2′-bipyridine), have been recognized and extensively exploited in the synthesis of various chemicals [5–11]. For example, the typical light-driven aerobic cross-dehydrogenative coupling (CDC) reaction of *N*-phenyltetrahydroisoquinoline derivatives with phosphite esters can be catalyzed by Ru^II or Ir^III-polypyridyl complexes to form medicinally important α-aminoquinoline phosphonates via single-electron transfer (SET) processes [6,12–15]. However, these homogeneous noble-metal photocatalysts will hinder their recycling and practical applications. In order to improve recyclability and reduce cost of such photocatalysts, it is effective to trap catalytic motifs into porous matrix [16].

Metal-organic frameworks (MOFs), a type of designable crystalline porous materials, can elucidate the interaction between host frameworks and catalytic centers at the atomic level with the help of single-crystal X-ray diffraction [17–34]. In particular, incorporation of Ru^II-polypyridyl complexes as catalytic active sites into MOFs has been proven to be attractive because of the outstanding chemical stability and high crystallinity of the resulting materials. Based on cation exchange or *in situ* synthesis, some MOFs with anionic hosts can support a [Ru^II(bpy)_3] photoredox catalyst. However, none of these MOFs showed a well-organized [Ru^II(bpy)_3] photoredox catalyst, which might hinder the mechanism study [19,21,26]. Moreover, almost all of [Ru^II(bpy)_3]-loaded MOFs show lower catalytic activity than a comparable amount of individual [Ru^II(bpy)_3] photoredox catalyst, because heterogeneous catalysis is more disadvantageous for mutual contaction between catalysts and substrates than homogeneous catalysis and the host framework itself is catalytically inactive [17,18,35]. Thus, optimizing the catalytic activity of [Ru^II(bpy)_3] photoredox catalyst in a heterogeneous catalytic system remains a challenge, and developing novel photoinduced electron transfer (PET) process during the photocatalytic process is highly desirable.

To address the above problems, the synergistic effect of radical porous host and [Ru^II(bpy)_3] photocatalyst is an effective strategy to optimal PET process. It has been reported that radicals are critical

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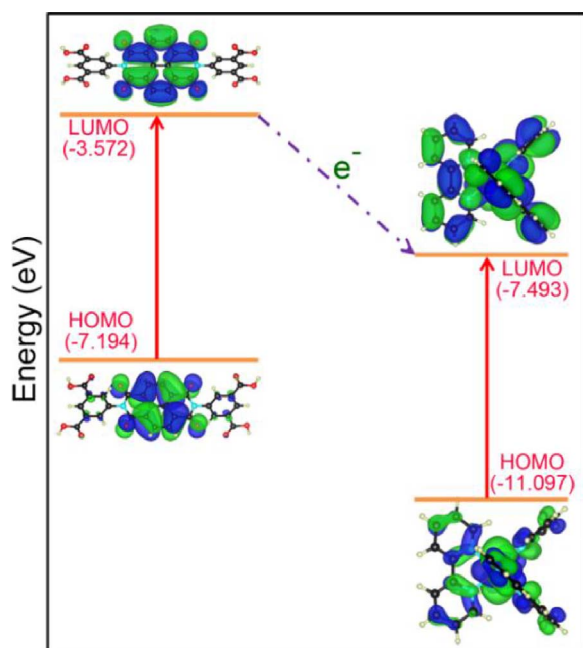[1] These authors contributed equally.

**Fig. 1.** HOMO-LUMO energy profiles of H$_4$BINDI (left) and [Ru$^{II}$(bpy)$_3$] (right).

intermediates in C−C or C−P bond formation driven by visible light [36–38]. 1,4,5,8-Naphthalenediimide (NDI), which can undergo reversible single-electron reduction to form stable radical anions served as redox-active units, has been considered as an excellent type of organic linker in the construction of photoelectronically active MOFs. However, the photocatalytic properties of the MOFs based on NDI-type organic linkers have been rarely investigated [39–44], which inspires us to explore the synergistic effect of NDI radicals and the [Ru$^{II}$(bpy)$_3$] photoredox catalyst in photocatalysis.

We question whether some novel PET pathways between NDI and [Ru$^{II}$(bpy)$_3$] photocatalyst will happen through the redox reactions of their excited state? Density functional theory (DFT) calculations were performed on H$_4$BINDI and [Ru$^{II}$(bpy)$_3$] to verify the possibility. DFT calculations (Fig. 1) show that the lowest unoccupied molecular orbital (LUMO) of H$_4$BINDI fragment (−3.572 eV) lies in higher energy than the LUMO of [Ru$^{II}$(bpy)$_3$] (−7.493 eV), indicating the efficient electron transfer may occur from H$_4$BINDI to [Ru$^{II}$(bpy)$_3$] [40,45]. The proposed redox process is also consistent with the redox potentials of key intermediates (i.e., Ru$^{II}$ as oxidant: E$_1$ = −1.47 V $vs$ Fc/Fc$^+$; NDI as reductant: E$_2$ = −1.83 V $vs$ Fc/Fc$^+$, Fig. S1). Hence, the synergistic effect of NDI radicals and the [Ru$^{II}$(bpy)$_3$] photoredox catalyst in visible-light-driven photocatalysis is certainly worth exploring. Moreover, we construct anionic NDI-based MOFs bearing [Ru$^{II}$(bpy)$_3$] photoredox catalyst as a charge-balanced cation (Scheme 1) and disclose an unprecedented PET pathway combining NDI radical and [Ru$^{II}$(bpy)$_3$] photoredox catalyst.

In this paper, two three-dimensional (3D) porous MOFs, [Mn$_3$(BINDI)$_2$(H$_2$O)$_2$Cl]·3Me$_2$NH$_2$ (**FJI-Y1**, **FJI** = Fujian Institute, H$_4$BINDI = *N*,*N'*-bis(5-isophthalate acid)naphthalene-diimide) and [Mn$_6$(BINDI)$_4$(H$_2$O)$_2$Cl$_2$]·[Ru$^{II}$(bpy)$_3$]·4Me$_2$NH$_2$ (**FJI-Y2**) are

constructed, which have similar Kagomé lattices pillared by NDI groups. For the typical visible-light-driven CDC reactions, the heterogeneous [Ru$^{II}$(bpy)$_3$]-loaded **FJI-Y2** shows high isolated yield of 80%, which is about 1.43 times enhancement over that of the homogeneous [Ru(bpy)$_3$]Cl$_2$. The effective heterogeneous photocatalysis reflects that the multiple intermolecular interactions between [Ru$^{II}$(bpy)$_3$] and NDI radicals in the framework induce optimal PET process to expedite chemical conversion and recycling of catalysts.

## 2. Experimental

### 2.1. Materials and methods

Commercially available reagents were used as received. Thermal gravimetric analysis data were obtained with a NETZSCH STA 449C analyzer. All samples and reference material (Al$_2$O$_3$) were enclosed in a platinum crucible and were heated from 25 °C to 800 °C at a rate of 10 °C/min under N$_2$ atmosphere. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Mini 600 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) at a scanning rate of 5°/min for 2θ ranging from 4° to 40°. Simulated XRPD patterns were calculated using *Mercury* from the single-crystal structural models. Routine $^1$H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.1 MHz for $^1$H NMR). The deuterated solvents used are indicated in the experimental details. Optically diffuse reflectance spectra were measured at room temperature on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer. EPR spectra were recorded on a Bruker BioSpin E500 EPR spectrometer equipped with a 16 mW ultraviolet lamp and using a 100 kHz magnetic field modulation at room temperature. Electrochemical measurements are performed by CV (cyclic voltammetry) CHI760. Elemental mapping analysis was conducted by using a SU-8010 scanning electron microscope.

### 2.1.1. Preparation of [Mn$_3$Cl(BINDI)$_2$(H$_2$O)]·3Me$_2$NH$_2$·xguest (FJI-Y1)

0.05 mmol H$_4$BINDI (30 mg), 0.25 mmol MnCl$_2$·4H$_2$O (57 mg), 0.2 ml 4 M HCl and 4 ml DMA were sealed and dissolved in an 8 ml vial, and then heated in an oven at 120 °C for 72 h. The vial was then allowed to cool to room temperature. After washing with fresh DMA, orange crystals were obtained (Yield: 36 mg, 68%, based on H$_4$BINDI).

### 2.1.2. Preparation of [Mn$_6$(BINDI)$_4$(H$_2$O)$_2$Cl$_2$]·[Ru$^{II}$(bpy)$_3$]·4Me$_2$NH$_2$·xguest (FJI-Y2)

0.05 mmol H$_4$BINDI (30 mg), 0.25 mmol MnCl$_2$·4H$_2$O (57 mg), 0.02 mmol [Ru(bpy)$_3$]Cl$_2$ (15 mg), 0.2 ml 4 M HCl and 4 ml DMA were sealed in an 8 ml vial and heated in an oven at 120 °C for 72 h. Then the vial was allowed to cool to room temperature. After washing with fresh DMA, red crystals were obtained (Yield: 39 mg, 66%, based on H$_4$BINDI).

### 2.2. X-ray crystallography

Diffraction data of **FJI-Y1** and **FJI-Y2** were collected on a SuperNova diffractometer equipped with a copper micro-focus X-ray source (λ = 1.5406 Å) and an Atlas CCD detector. The structure was solved by direct methods and refined with full-matrix least-squares technique using *SHELXL*-2016 [46]. All non-hydrogen atoms were refined with anisotropic
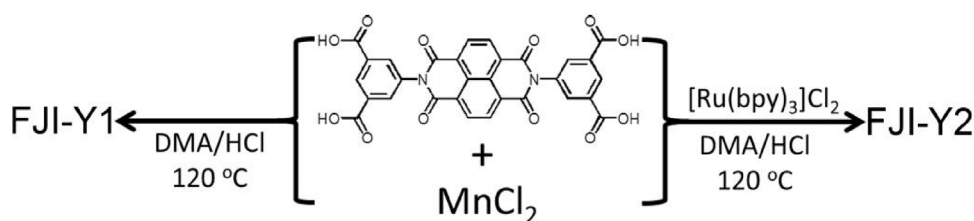
**Scheme 1.** Synthesis of **FJI-Y1** (left) and **FJI-Y2** (right) by using H$_4$BINDI ligand and MnCl$_2$ in the absence and presence of [Ru(bpy)$_3$]Cl$_2$, respectively.



FJI-Y1 ← DMA/HCl 120 °C  [+ MnCl$_2$]  [Ru(bpy)$_3$]Cl$_2$ DMA/HCl 120 °C → FJI-Y2

displacement parameters. The diffuse electron densities resulting from residual solvent molecules were removed from the dataset using the SQUEEZE routine of PLATON and the data generated were refined further [47]. The contents of the solvent region are not represented in the unit cell contents in the crystal data. ***Crystal data of FJI-Y1:*** $C_{70}H_{53}N_8O_{26}ClMn_3$ ($M_r = 1622.47$): monoclinic, space group $P2_1/c$, $a = 18.6552(3)$ Å, $b = 21.15630(10)$ Å, $c = 33.4582(5)$ Å, $\beta = 127.765(2)°$, $V = 10439.0(3)$ Å$^3$, $Z = 4$, $T = 100.0(5)$ K, $\mu = 3.665$ mm$^{-1}$, $D_{calc} = 1.032$ g/cm$^3$, 190816 reflections measured ($6.684° \leq 2\theta \leq 146.81°$), 20808 unique ($R_{int} = 0.0503$, $R_{sigma} = 0.0230$) which were used in all calculations. The final $R_1$ was 0.0754 ($I > 2\sigma(I)$) and $wR_2$ was 0.2238 (based on all data). ***Crystal data of FJI-Y2:*** $C_{154}H_{80}N_{17}O_{50}Cl_2Mn_6Ru$ ($M_r = 3455.95$): monoclinic, space group $P2_1/c$, $a = 31.4652(7)$ Å, $b = 21.1868(6)$ Å, $c = 33.7591(6)$ Å, $\beta = 109.053(2)°$, $V = 21272.5(9)$ Å$^3$, $Z = 4$, $T = 100.1(2)$ K, $\mu = 4.164$ mm$^{-1}$, $D_{calc} = 1.079$ g/cm$^3$, 69919 reflections measured ($6.796° \leq 2\theta \leq 142.252°$), 38953 unique ($R_{int} = 0.0482$, $R_{sigma} = 0.0675$) which were used in all calculations. The final $R_1$ was 0.1024 ($I > 2\sigma(I)$) and $wR_2$ was 0.3083 (based on all data).

### 2.3. Typical experimental procedure for catalysis

Catalyst **FJI-Y2** (1.0 mmol% based on [Ru$^{II}$(bpy)$_3$]) and the respective substrate (0.2 mmol) in dry MeCN (0.4 ml) were added to a 10 ml Schleck flask. Then phosphite esters (2.0 equiv.) was added with very slowly stirring and the reaction mixture was placed about 10 cm from a 14 W fluorescent lamp. Upon the completion of reaction after 12 h, as monitored by TLC (petroleum ether/EtOAc = 5:1), the crude reaction mixture was purified by flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/EtOAc (3:1–2:1) to provide the pure product.

### 2.4. Electrochemical measurements

The redox potentials of the H$_4$BINDI and [Ru(bpy)$_3$]Cl$_2$ were measured using a three-electrode cell at room temperature. A platinum electrode was used as the working electrode, platinum wire as the counter electrode, and a platinum wire as the reference. Electrochemical measurements of the analytes were carried out using 0.01 mmol solutions of tetrabutylammonium hexafluorophosphate solution in acetonitrile. The powdered materials were coated on 3 mm wide platinum electrode. The reduction potentials of the compounds were obtained from the cyclic voltammograms and corrected with respect to the Fc/Fc$^+$ internal standard.

### 2.5. Molecular simulations and DFT calculations

To quantitatively evaluate the interactions between BINDI ligands and [Ru$^{II}$(bpy)$_3$] cations, their electronic properties were calculated using DFT. All molecules were optimized using the B3PW912 hybrid functional with 6–31G(d) basis set. The HOMO and LUMO energy levels of BINDI ligand and [Ru$^{II}$(bpy)$_3$] cation were calculated using the B3PW91 hybrid function with 6–311G** basis set. The B3PW91 function was developed by Becke [48] and demonstrated to be computationally accurate and fast for bandgap calculations [49]. All the calculations were carried out using Gaussian 09.

## 3. Results and discussion

### 3.1. Crystal structure

Orange single crystals of **FJI-Y1**, formulated as [Mn$_3$Cl (BINDI)$_2$(H$_2$O)]·3Me$_2$NH$_2$·$x$guest, are obtained by a solvothermal reaction of MnCl$_2$, H$_4$BINDI in $N,N'$-dimethylacetamide (DMA) at 120 °C for 72 h. Single-crystal X-ray diffraction reveals that compound **FJI-Y1** crystallizes in the monoclinic space group $P2_1/c$. One prominent structural feature in **FJI-Y1** is the presence of Kagomé lattices, whose formation is closely related to two types of building units (Fig. 2a and Fig. S2). One is the extraordinary anionic [Mn$_2$(COO)$_4$Cl$_2$]$^{2-}$ paddle-wheel unit (SBU1) with two square-pyramidal Mn$^{II}$ ions bonded by four carboxyl groups and two terminal Cl$^-$ ligands. In the second anionic unit [Mn$_2$(COO)$_6$(H$_2$O)]$^-$ (SBU2), one Mn$^{II}$ cation is surrounded by five O atoms from four carboxyl groups to complete the square-pyramidal
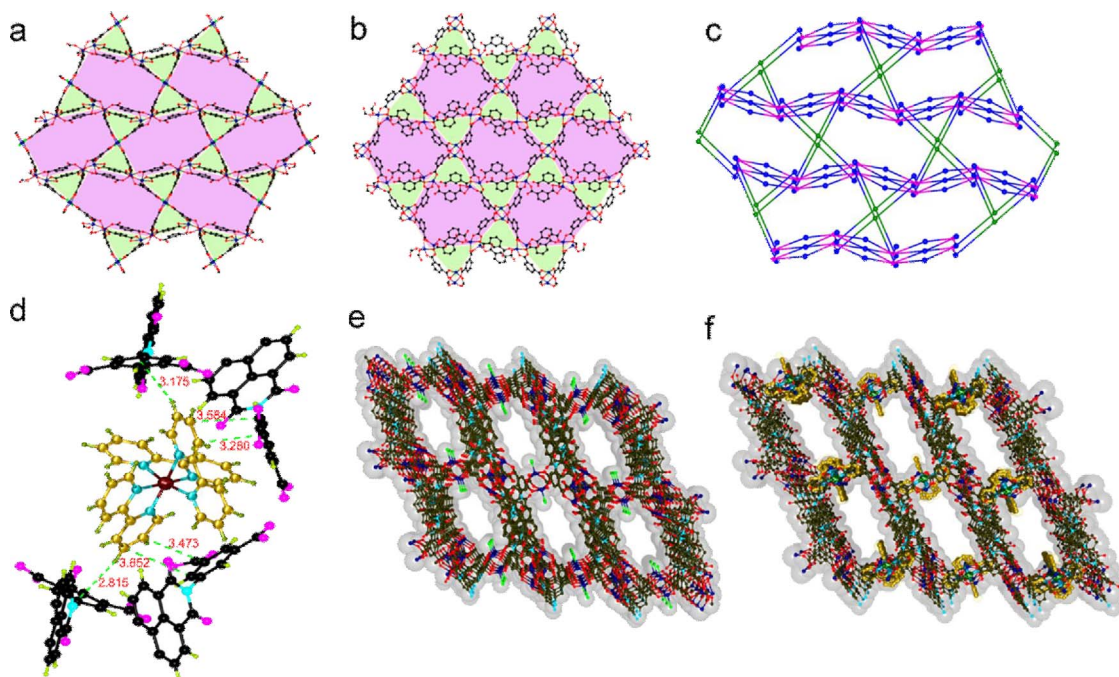


**Fig. 2.** Structural representations of **FJI-Y1** and **FJI-Y2**. Kagomé lattices in (a) **FJI-Y1** and (b) **FJI-Y2**. (c) (4,6)-connected net in **FJI-Y1** and **FJI-Y2**. (d) Multiple intermolecular interactions between BINDI ligands and [Ru$^{II}$(bpy)$_3$] cations in **FJI-Y2**. 3D porous frameworks of (e) **FJI-Y1**, and (f) **FJI-Y2**, viewed along the $b$ axis, [Ru$^{II}$(bpy)$_3$] cations encapsulated in pores are highlighted as yellow atoms. Note: all coordinated solvent molecules and dissociative [Me$_2$NH$_2$]$^+$ cations are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

coordination geometry. Meanwhile, the other distorted octahedral Mn$^{II}$ cation is coordinated by four carboxyl O atoms and one terminal H$_2$O. There are hydrogen bonds with N−H⋯O lengths of 2.74 Å to 2.94 Å and angles of 156.09° to 174.02° between the O atoms of coordinated H$_2$O or carboxyl groups and charge-balanced [Me$_2$NH$_2$]$^+$ cations derived from the decomposition of DMA solvent (Fig. S2). One SBU1 unit and two SBU2 units are connected by four isophthalate sections in BINDI ligands to form a three-membered ring, and four SBU2 units and two SBU1 units are connected by eight isophthalate sections in BINDI ligands to form a six-membered ring. Finally, the connection of these three- and six-membered rings by sharing edges further extends the structure into a two-dimensional layer with Kagomé topology (Fig. 2a) [50]. The edge lengths in the Kagomé lattices are 9.37 Å to 10.83 Å. These Kagomé lattices as super secondary building units are further linked to other two adjacent Kagomé lattices by the remaining NDI groups of BINDI ligands along *a* direction, generating a 3D porous anionic pillar-layer motif with one-dimensional (1D) channels along the *a* and *b* axes (Fig. 2e and Fig. S3). These channels with a window size of about $9 \times 11\ Å^2$ (atom to atom distance) are filled with disordered solvent molecules and charge-balancing [Me$_2$NH$_2$]$^+$ cations. Topologically, the framework of **FJI-Y1** can be described as a (4,6)-connected net with stoichiometry of (4-c)$_5$(6-c)$_2$ by reducing each SBU1 unit, SBU2 unit and BINDI ligand as the 4-, 6- and 4-connected nodes, respectively (Fig. 2c).

Red single crystals of **FJI-Y2**, formulated as [Mn$_6$(BINDI)$_4$(H$_2$O)$_2$Cl$_2$]·[Ru$^{II}$(bpy)$_3$]·4Me$_2$NH$_2$·$x$guest, are obtained from the similar reaction of **FJI-Y1**, in the presence of [Ru(bpy)$_3$]Cl$_2$. Single-crystal X-ray diffraction reveals that compound **FJI-Y2** has similar (4,6)-connected network with Kagomé lattices pillared by NDI section of the BINDI ligands. Interestingly, there are two kinds of charge-balanced cations. One is the common [Me$_2$NH$_2$]$^+$, and another one is the extraordinary photocatalyst [Ru$^{II}$(bpy)$_3$] located in the pores (Fig. S5). Although some MOFs have been reported to capture [Ru$^{II}$(bpy)$_3$] cations into their pores by solvent-assisted cation exchange or synthesis *in situ* [19,35,51–55], the distinct structure of [Ru$^{II}$(bpy)$_3$] in framework is often hard to determine due to severe disorder and partial occupy. Furthermore, these [Ru$^{II}$(bpy)$_3$] cations in **FJI-Y2** are considered to be uniform and accessible catalytic centers that enhance catalytic activity by eliminating the deactivation pathways caused by agglomeration of catalyst. These [Ru$^{II}$(bpy)$_3$] cations are restricted in the pores by multiple intermolecular interactions, such as short C−H⋯π lengths of 3.105 Å and 3.142 Å measured as the distance between the H atoms and the phenyl centroids, and slipped π stacking with lengths of 3.297 Å to 3.791 Å measured as the distance between two C atoms from the phenyl rings of BINDI ligands and pyridine rings of [Ru$^{II}$(bpy)$_3$] cations (Fig. 2d). In **FJI-Y2**, the [Mn$_2$(COO)$_4$Cl$_2$]$^{2-}$ paddle-wheel unit is similar to that of **FJI-Y1**. However, the presence of such large [Ru$^{II}$(bpy)$_3$] cations leads to the rotation of BINDI ligands, and further affects the coordination geometries of Mn(II) and BINDI ligands in two

crystallographically independent [Mn$_2$(COO)$_6$(H$_2$O)$_2$]$^-$ units (Fig. S4), in which some hydrogen bonds with N−H⋯O lengths of 2.64 Å to 2.83 Å and angles of 153.02° to 169.19° between the O atoms from carboxyl groups and [Me$_2$NH$_2$]$^+$ cations can also be seen. Thus, compared to **FJI-Y1**, the Kagomé lattices in **FJI-Y2** are obviously twisted (Fig. 2b). Despite encapsulation of large [Ru$^{II}$(bpy)$_3$] cations, the structure of **FJI-Y2** generates 1D channels with a window size of about $8 \times 12\ Å^2$ (atom to atom distance) along the *b* axis (Fig. 2f).

The as-synthesized samples of both MOFs are crystal particles, not powder. To further testify their phase purity, a mass of wet crystals of **FJI-Y1** and **FJI-Y2** are ground and used for powder X-ray diffraction (PXRD) measurement, respectively. Compared to the simulated PXRD patterns of host frameworks, the presence of some additional weak peaks is attributable to the poor backgrounds induced by solvent in the pores and on the surface of both crystalline samples. For facilitate catalysis, high porosity and open channels are crucial for efficient transport of substrate and product molecules. However, the expected experimental Brunauer-Emmett-Teller (BET) surface areas can't be supported by N$_2$ adsorption measurements because of framework collapse upon solvent removal, which is a common phenomenon observed for many porous MOFs. Despite that, the PXRD patterns of fresh wet samples of **FJI-Y1** and **FJI-Y2** (Figs. S7 and S8) indicate their stabilities in DMA and MeCN, which is very important for the following photocatalysis. To better understand both pore structures, their pore parameter is estimated using the Zeo+ + software.[56] The solvent accessible volumes of **FJI-Y1** and **FJI-Y2** without all of the coordinated and dissociative solvent molecules are about 43.3% and 38.2% of the total crystal volume, according to the theoretical pore volumes of 0.44 and 0.36 cm$^3$/g, respectively. Their estimated surface areas are 1455 and 1210 m$^2$/g, respectively. The simulated pore size distribution (PSD) for **FJI-Y2** shows a dominating distribution of micropores at 8.3–9.7 Å, which is similar to that of **FJI-Y1** (Fig. S9).

### 3.2. Optical property

As shown in Fig. 3, **FJI-Y1** is stable in air and sensitive to sunlight, leading to a photochromic transformation from orange to dark green (**FJI-Y1a**) upon irradiation by sunlight for several minutes. The orange color returns after several hours in the darkness. After being soaked in the MeCN solution of *N*-phenyltetrahydroisoquinoline (**A**), orange **FJI-Y1** can also turn into another dark green material (**FJI-Y1b**) upon irradiation with visible light. PXRD reveals that the crystal structures of **FJI-Y1a** and **FJI-Y1b** are identical to that of **FJI-Y1**. The NDI moiety is known to be redox-active and can generate radicals upon light irradiation (Fig. S10). Such chromism suggests that the photoresponsive behaviours may result from an electron-transfer chemical process in the structure without structural transformation [40]. As shown in Fig. 4c, the UV/Vis spectrum of **FJI-Y1** shows a strong absorption band at 390 nm, corresponding to the n–π* and π–π* transition of aromatic
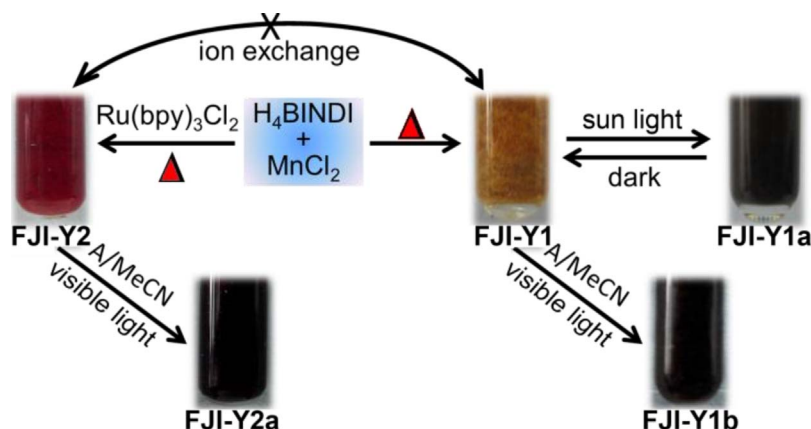
**Fig. 3.** Light induced photochromism of **FJI-Y1** and **FJI-Y2** under the irradiation of visible light. (**A** = *N*-phenyltetrahydroisoquinoline).
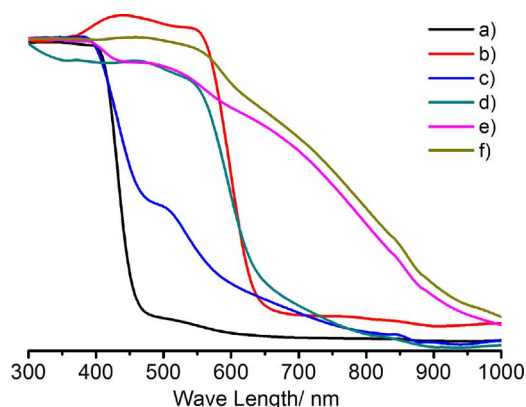
**Fig. 4.** Solid state UV–vis spectra. (a) H4BINDI, (b) [Ru^II(bpy)₃]Cl₂, (c) **FJI-Y1**, (d) **FJI-Y2**, (e) **FJI-Y1b**, (f) **FJI-Y2a**.

BINDI ligands [39,40], and which can also be seen in the UV/Vis spectrum of H4BINDI ligands (Fig. 4a). The band gap energy of **FJI-Y1** is 2.24 eV calculated from UV–vis data. However, the UV–vis spectrum of **FJI-Y1b** shows an abrupt change in absorption band which reveals that reversible photochromism may result from a photo-induced electron-transfer chemical process inside the structure (Fig. 4e) [36,37,40], giving its band-gap energy of 1.25 eV (Fig. 4e). The spectrum of **FJI-Y2** displays a transformation of the shoulder peak at 501 nm, into a broad band in the region of 510–830 nm, which is similar to that of photocatalyst [Ru(bpy)₃]Cl₂ (Fig. 4b and d). The band-gap energy of **FJI-Y2**, calculated from UV–vis data is 1.86 eV. After being immersed in a solution of **A** in MeCN and irradiated with visible light, red **FJI-Y2** can also turn into another dark red species (**FJI-Y2a**) without structural transformation, as confirmed by PXRD measurements (Figs. 3 and S8). Compared to **FJI-Y2**, the absorption edge of **FJI-Y2a** is red shifted and the band-gap energy is reduced to 1.24 eV because of the photo-responsive behaviour resulting from an electron-transfer chemical process between the [Ru^II(bpy)₃] cations and BINDI ligands (Fig. 4f).

### 3.3. CDC reaction of N-phenyltetrahydroisoquinoline (A) with phosphite esters (B)

Based on the above results, we become interested in the development of a novel SET pathway between NDI radicals and [Ru^II(bpy)] photocatalysts by using the typical CDC reaction of *N*-phenyltetrahydroisoquinoline (**A**) with phosphite esters (**B**) as a probe reaction. This will demonstrate the utility and applicability of photoredox catalysis in organic chemistry. As shown in Table 1, the controlled experiments indicate that light, oxygen and the MOF photocatalyst are all necessary for such typical CDC reaction (Entries 1, 3, 6 and 7; Table 1). Employing **FJI-Y1** as catalyst (Entry 4; Table 1), the reaction affords desired product α-aminophosphonate (**C**) with an isolated yield of 7% after 12 h. This yield is much lower than that (56%) of homogeneous 1 mmol% [Ru(bpy)₃]Cl₂ catalyst (Entry 2; Table 1). For **FJI-Y2** (1 mmol% based on [Ru^II(bpy)₃]), the isolated yield of the reaction after 12 h is up to 80% (Entry 8; Table 1), which is much higher than that produced by 1 mmol% [Ru(bpy)₃]Cl₂ as homogeneous catalyst, and also higher than that (62%, Entry 5; Table 1) of mixed catalysts of [Ru(bpy)₃]Cl₂ and **FJI-Y1**. This is an extraordinary phenomenon for a photocatalytic process catalyzed by MOFs. Although some [Ru^II(bpy)₃]-loading MOFs were employed as photocatalysts in aerobic oxidative reactions, most of them showed lower catalytic activity than a comparable amount of individual [Ru^II(bpy)₃]Cl₂ photoredox catalyst due to the untoward contaction between catalyst and substrates in heterogeneous catalysis and the absence of PET between porous host and [Ru^II(bpy)₃]. For catalyst **FJI-Y2**, the multiple intermolecular interactions between [Ru^II(bpy)₃] cations and BINDI ligands with NDI radicals are conducive

to optimal PET process promoting the photocatalytic conversion of chemical bonds in the aerobic CDC reaction. In addition, elemental mapping analysis (Fig. S11) indicates the spatial distribution of well-defined [Ru^II(bpy)₃] cations in **FJI-Y2** is uniform catalytic centers accessible to enhanced catalytic activity by elimination of the deactivation pathways caused by agglomeration of [Ru^II(bpy)₃] catalyst [57].

Removal of the catalyst after 4 h (yield: 29%, Entry 9; Table 1) results in no further production **C** after a further 8 h of irradiation (Entry 10; Table 1), indicating the heterogeneous nature of catalyst **FJI-Y2**. The reusability of the catalyst **FJI-Y2** is then investigated as shown in Table 2. The same batch of catalyst **FJI-Y2** is used over three successive catalytic cycles. The results indicate that the catalytic efficiency of **FJI-Y2** is no significant loss after three cycles. In addition, PXRD measurements of the recycled **FJI-Y2** reveal maintenance of its crystalline structure and framework, confirming the stability of framework in the catalytic system (Fig. S8).

To investigate the generality of this aerobic CDC reaction catalyzed by **FJI-Y2**, the substrate scope is examined and the results are shown in

**Table 1**
The visible light induced aerobic CDC reactions of *N*-phenyltetrahydroisoquinoline (**A**) with diethyl phosphite (**B**) catalyzed by different catalysts.[a]

| Entry | Catalyst | Time/hour | Yield/%[b] |
|---|---|---|---|
| 1 | None | 12 | trace |
| 2 | [Ru(bpy)₃]Cl₂ | 12 | 56 |
| 3[c] | [Ru(bpy)₃]Cl₂ | 12 | trace |
| 4 | **FJI-Y1** | 12 | 7 |
| 5 | [Ru(bpy)₃]Cl₂ + **FJI-Y1** | 12 | 62 |
| 6[d] | **FJI-Y2** | 12 | trace |
| 7[e] | **FJI-Y2** | 12 | trace |
| 8 | **FJI-Y2** | 12 | 80 |
| 9 | **FJI-Y2** | 4 | 29 |
| 10[f] | **FJI-Y2** | 4 + 8 | 29 |

[a] Reaction conditions: substrate **A** (0.2 mmol), diethyl phosphite **B** (0.4 mmol), catalysts (1 mmol%) in 0.4 ml MeCN exposed to air with visible light irradiation at room temperature.
[b] Isolated Yield.
[c] The reaction in the presence of [Ru(bpy)₃]Cl₂ was stirred under the dark and air atmosphere.
[d] The reaction in the presence of **FJI-Y2** was stirred under the dark and air atmosphere.
[e] The reaction mixture was strictly degassed and then irradiated under an Ar atmosphere.
[f] Filtration testing by removing the catalyst **FJI-Y2** after 4 h and continuing the reaction for another 8 h.

**Table 2**
The visible light induced aerobic CDC reactions of *N*-phenyltetrahydroisoquinoline derivatives (**A**) with phosphite esters (**B**) catalyzed by catalyst **FJI-Y2**.[a]

| Entry | −R₁ and −R₂ | Yield/%[b] |
|---|---|---|
| 1 | -H and −Me | 82/81/78 |
| 2 | -Me and −Me | 78/76/75 |
| 3 | -OMe and −Me | 84/82/82 |
| 4 | -Br and −Me | 89/88/87 |
| 5 | -H and −Et | 80/78/76/75/71[c] |
| 6 | -Me and −Et | 77/75/73 |
| 7 | -OMe and −Et | 85/83/75 |
| 8 | -Br and −Et | 86/85/85 |
| 9 | -H and i-Pr | 69/67/67 |
| 10 | -Me and i-Pr | 62/61/61 |
| 11 | -OMe and i-Pr | 66/65/66 |

[a] Reaction conditions: substrate **A** (0.2 mmol), phosphite esters **B** (0.4 mmol), catalyst **FJI-Y2** (1 mmol% based on [Ru^II(bpy)₃]) in 0.4 ml MeCN exposed to air with visible light irradiation at room temperature for 12 h.
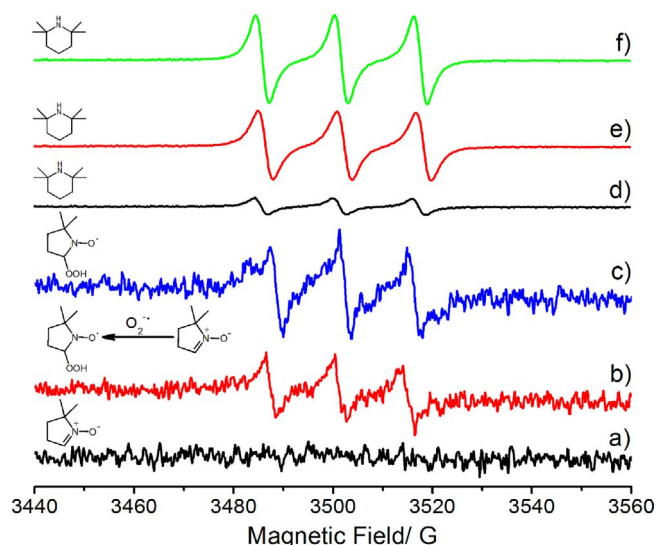[b] Isolated yields for the first three runs.
[c] Five cycles have been done.

**Fig. 5.** EPR spectra of CH$_3$CN solution with DMPO (a); with **FJI-Y2** and DMPO (b); with **FJI-Y2**, **A** and DMPO (c) under irradiation of visible light for 60 min. EPR spectra of CH$_3$CN solution with TEMP (d); with **FJI-Y2** and TEMP (e); with **FJI-Y2**, **A** and TEMP (f) under irradiation of visible light for 60 min.

Table 2. It can be observed that various substituted tetra-hydroisoquinoline derivatives can undergo aerobic CDC reactions with diethyl phosphite, catalyzed by **FJI-Y2** under visible light, giving the coupling products in good to excellent yields (Entries 5–8; Table 2). It is also observed that various substituted tetrahydroisoquinolines can undergo aerobic CDC reactions with smaller dimethyl phosphite (Entries 1–4; Table 2) and bigger isopropyl phosphite (Entries 9–11; Table 2) catalyzed by photocatalyst **FJI-Y2** under visible light. As the sizes of substituent groups in phosphite esters increase, the yields decrease because large substituent groups hinder the contaction between two substrates.

To understand the photocatalytic process of **FJI-Y2** in detail, the electron paramagnetic resonance (EPR) spectroscopy measurements are conducted in 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) for capture of superoxide radical anion O$_2{}^-$· and singlet oxygen $^1$O$_2$, respectively. As shown in Fig. 5, upon irradiation of the CH$_3$CN mixture of **FJI-Y2** and DMPO in air, generated O$_2{}^-$· under the reaction condition reacts with DMPO to form final superoxide, which is confirmed by EPR spectroscopy (Fig. 5b). As shown in Fig. 5d–f, no $^1$O$_2$ can be generated during the photocatalysis process. These findings indicate that O$_2{}^-$· is the active intermediate species in the reaction. It is noted that the differences in above peak intensities are mainly caused by the different dose of tested solvent, which is very hard to control by using capillary for sampling.

In an effort to understand the catalytic reaction, we postulate the reaction mechanism shown in Scheme 2. Upon irradiation by visible light, the NDI groups in **FJI-Y2** are converted to the excited state NDI*, which is immediately quenched by the visible light excited Ru$^{II*}$ *via* a novel SET process to generate a low-valent Ru$^I$ complex and the radical cation NDI$^+$·. Molecule **A** transfers an electron to the radical cation NDI$^+$· to form the radical anion **A**$^+$·, and simultaneously reduces NDI$^+$· to its ground state, while the Ru$^I$ complex turnover can be accomplished by the reduction of oxygen [O] to the superoxide radical anion [O]$^-$·. These [O]$^-$· may abstract a hydrogen atom from the radical cation **A**$^+$· to form the desired iminium ion. Addition of nucleophile to the iminium ion leads to the desired product. Such novel photoinduced SET process between NDI radical and [Ru$^{II}$(bpy)$_3$] photocatalyst may be correlative to the multiple intermolecular interactions (such as C—H···π and slipped π-π interactions) between [Ru$^{II}$(bpy)$_3$] cations and BINDI ligands in the host framework, affording
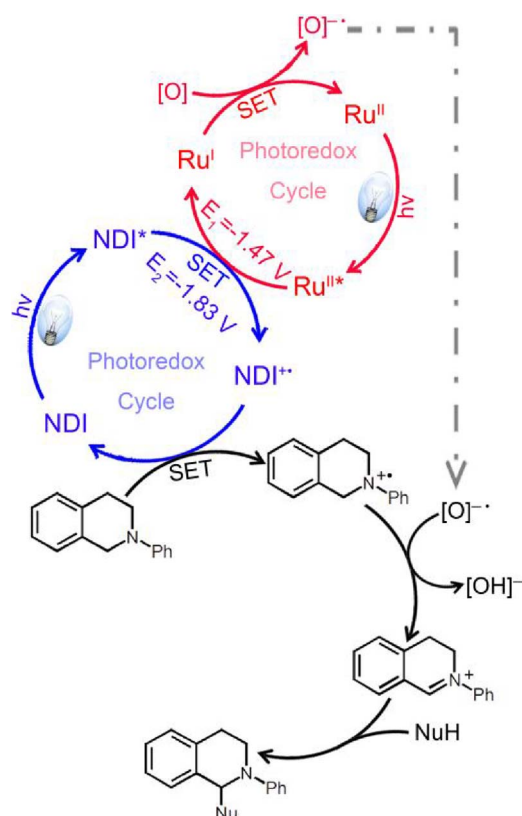


**Scheme 2.** Proposed cooperative catalysis mechanism of NDI radical (blue cycle) and [Ru$^{II}$(bpy)$_3$] photocatalyst (red cycle) via a novel SET pathway. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

optimal electron or energy transfer, expediting the recycling of two photoredox catalysts [52], and further promoting their catalytic activities. Furthermore, individual photocatalytic processes of BINDI ligand and [Ru$^{II}$(bpy)$_3$] photocatalyst (Schemes S1 and S2) can't be ignored.

## 4. Conclusions

In summary, we have for the first time combined 1,4,5,8-naphthalenediimide (NDI) radicals and [Ru$^{II}$(bpy)$_3$] photocatalysts into an anionic MOF, namely [Mn$_6$(BINDI)$_4$(H$_2$O)$_2$Cl$_2$]·[Ru$^{II}$(bpy)$_3$]·4Me$_2$NH$_2$ (**FJI-Y2**), which is described as a novel (4,6)-connected net consisted of Kagomé lattices with redox-active NDI groups as pillars. Molecular simulations and DFT calculations indicate that multiple intermolecular interactions (such as C—H···π and slipped π-π interactions) between NDI radicals and photoredox catalysts [Ru$^{II}$(bpy)$_3$] contribute to optimal photoinduced SET process promoting the photocatalytic conversion of chemical bonds and expediting the recycling of catalysts. Such extraordinary catalytic mechanism has been demonstrated by the typical aerobic CDC reactions of *N*-phenyltetrahydroisoquinoline and its derivatives with phosphite esters. The catalytic activity of the recycled [Ru$^{II}$(bpy)$_3$]-loading **FJI-Y2** is about 1.43 times enhancement over that of homogeneous photocatalyst [Ru(bpy)$_3$]Cl$_2$, and the best yield of medicinally important α-Aminoquinoline phosphonates can be reached up to 89%. These results indicate that MOFs containing radicals can be ideal platforms to incorporate more noble-metal photocatalysts for promoting photocatalysis.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apcatb.2018.01.048.

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